

A method of more correct detection of the shortest atomic distances in liquid metals

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Abstract. The results of modeling of the structure factors (SF) and radial distribution functions (RDF) of atoms for a number of liquid metals with the close-packed crystal lattices are discussed. The special attention is paid to the most detailed coincidence of the experimental and calculated SF curves at their high-angle region. The shortest atomic distance values r_1^{SF} found from the SFs were shown to be smaller by some per cents than the values r_1^{RDF} determined as the abscissa of the RDF first peak and than the shortest distances in a crystalline state. It was determined that the high-angle part of the experimental SF curve may be reproduced satisfactorily by the model curve only when the first atomic coordination includes not a single but two or three predominant distances (r_1 , r_2 and r_3) between atoms.

1. Introduction

The atomic structure of liquid metals is usually studied by the diffraction methods. The initial data obtaining from the experiment are the structure factor (SF) curves. As a rule, they have insignificant distinctions in publications of different authors. By means the Fourier-transformation method the radial distribution functions (RDF) of atoms are calculated from the SF curves. They are usually used for determination of the short range order parameters of a melt such as the shortest atomic distance r_1^{RDF} and the first coordination number z_1 . The size of the ordered groups of atoms and the following coordination spheres radii may be found also. The most important of these values is the distance between the nearest atomic neighbours because its comparison with the corresponding value in a crystal state is the basis for the conclusions on a mechanism of a crystal lattice destruction during the melting. But reported r_1 values obtained by various authors differ from each other essentially. They may be both longer and shorter comparatively to crystal distance r_1^c . So the necessity of more correct detection of the shortest atomic distances in liquid metals is obvious.

2. Theoretic analysis and calculation method

The r_1^{RDF} value corresponding to the first maximum peak abscissa depends on the kind of the RDF presentation: the total function $G(r) = 4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 g(r)$, the difference function $D(r) = 4\pi r^2 [\rho(r) - \rho_0]$ or the probability function $g(r) = \rho(r) / \rho_0$. Here, $\rho(r)$ and ρ_0 are the local and the average atomic densities of the melt correspondingly. The first and the second forms of RDF give the r_1^{RDF} values larger by 2-3 % than the third one. The displacement of the first peak toward larger distances depends on r^2 multiplier presence in these two RDF forms.

The next significant reason of the errors in the r_1^{RDF} detection is a truncation of an experimental SF curves $a(s)$ at the high-angle scattering region. Here, s is a wave vector module. One of the truncation effects is a displacement of the RDF first peak to larger atomic distances. This displacement appears

because substitution of the available experimental value s_h instead of infinity into the upper integration limit when the RDF is calculated using the Fourier-transformation method. For liquid metals the less is s_h the larger is r_1^{RDF} . To remove the truncation effects the extrapolating equation has been proposed [1]:

$$r_1^{\text{RDF}} = r_1^\infty + a \exp(-bs_h), \quad (1)$$

where a and b are constant values, characterizing the melt at a given temperature. Here, the distance r_1^∞ is considered to be the real most probable distance between the nearest atomic neighbours, free from the truncation effect errors. All of found r_1^∞ values in liquid close-packed metals according to equation (1) turned to be shorter than corresponding distances in a crystalline state near the melting point.

It was shown [2] that the influence of the s_h parameter on the r_1^{RDF} value depends on the presence of as a minimum two distinguishing predominant distances inside the first coordination sphere of liquid metals. These two or even three distances form partial coordination maxima which overlap and resulting abscissa permits to detect some average r_1^{RDF} value only. So, using the analysis of the first RDF maximum it is impossible to ascertain the inner structure of the first coordination in details.

This information may be ascertained by means of the simulation of the experimental SF using equation [3]

$$a(s) = 1 + \sum_{i=1}^n z_i \frac{\sin(sr_i)}{sr_i} \exp\left(-\frac{\bar{u}_i^2 s^2}{2}\right), \quad (2)$$

obtained in the assumption that the RDF curve of a liquid metal is a sum of the partial Gauss functions for a totality of coordination spheres

$$G(r) = 4\pi\rho_0 r^2 + \sum_{i=1}^n \frac{z_i}{\sqrt{2 \cdot \pi \cdot \bar{u}_i^2}} \left(\frac{r}{r_i}\right) \exp\left[-\frac{(r - r_i)^2}{2 \cdot \bar{u}_i^2}\right]. \quad (3)$$

Here, r_i , z_i and \bar{u}_i^2 are the radius of the i -th sphere, its coordination number and the root-mean-square displacement of atoms from their equilibrium positions.

According to equation (2) every coordination sphere of the melt in the scattering process produces the oscillating interference function. All of them decrease when the s parameter increases. The interference functions produced by the distant spheres (large r_i values) lower to zero already in the region of first to third maxima of SF. So the last maxima (usually fifth to sixth) of the curve depend on the diffraction at the shortest atomic distances exclusively.

Therefore to detect more correct values of the shortest distances in liquid metals it is necessary to obtain good coincidence of the experimental and calculated SF curves not only for high first maxima but especially in the high-angle region.

3. Calculation results and discussion

In accordance to equation (2) the SFs were calculated for a number of liquid metals with the close-packed structures (fcc, hcp and bcc) near their melting points using the experimental X-ray diffraction data [4]. During the simulation process the shortest distances r_1^{SF} were found to be smaller than r_1^{RDF} values for the melts under study. The examples of the experimental and calculated SF curves are represented in Figure 1 for liquid Al (fcc) and Li (bcc). We achieved the same good agreement between the experimental and simulation curves for other liquid metals. The results are given in Table 1. One can see that in all cases $r_1^{\text{SF}} < r_1^{\text{RDF}}$ and $r_1^{\text{SF}} < r_1^c$. The shortest distance reduction during the

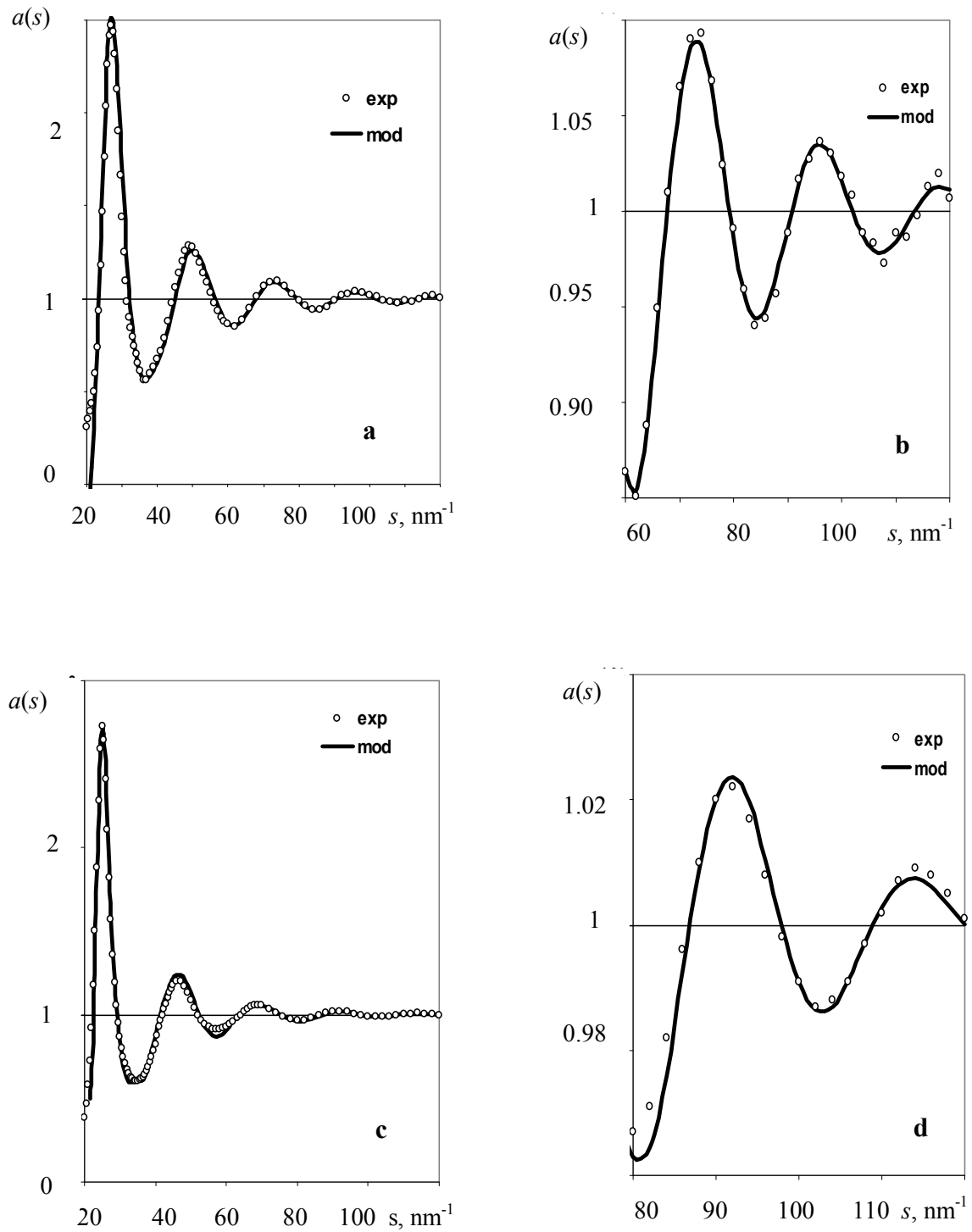


Figure 1. Experimental [4] and calculated structure factors of liquid Al (a, b) at $T = 943$ K and Li (c, d) at $T = 463$ K and high-angle parts of the curves (b, d)

Table 1. The first atomic distances found from RDF and SF curves in comparison with the corresponding crystal distances

Metal	T (K)	From $g(r)$		r_1 (nm) from $G(r)$	From SF			r_1^c (nm)
		r_1^{RDF} (nm)	r_1^∞ (nm)		r_1^{SF} (nm)	r_2^{SF} (nm)	r_3^{SF} (nm)	
Ni	1773	0.247	0.246	0.252	0.239	0.246	0.290	0.254
Co	1823	0.251	0.249	0.259	0.248	0.256	-	0.251
Cu	1423	0.253	0.253	0.260	0.249	0.276	0.300	0.261
Au	1423	0.278	0.275	0.282	0.267	0.290	0.323	0.293
Al	943	0.282	0.278	0.293	0.276	0.290	0.330	0.290
Ag	1273	0.283	0.281	0.295	0.269	0.290	0.319	0.295
Pb	613	0.329	0.325	0.335	0.320	0.348	0.400	0.350
Zn	723	0.268	0.267	0.275	0.260	0.287	0.327	0.270
Cd	623	0.299	0.294	0.317	0.288	0.306	-	0.299
Mg	953	0.311	0.309	0.322	0.289	0.318	-	0.320
Cr	2173	0.253	0.251	0.259	0.249	0.290	0.320	0.258
Fe	1833	0.258	0.255	0.263	0.253	0.260	-	0.254
V	2173	0.278	0.276	0.282	0.266	0.283	0.328	0.269
Li	463	0.298	-	0.307	0.287	0.309	0.350	0.304
Zr	2173	0.314	0.312	0.324	0.309	0.313	0.364	0.316
Ti	1973	0.316	0.315	0.323	0.265	0.315	0.320	0.289

melting process found from the SF simulation procedure is more noticeable than that from the RDF analysis. Besides, good agreement between the experimental and calculated SFs has been achieved at the high-angle region when two or three the most probable distances were taken into account. The r_1^{RDF} and r_1^∞ distances represent some intermediate quantity between them. For liquid Ti, V and Fe the r_1^{RDF} values were found to be larger than in the crystalline state. However, the r_1^{SF} quantities turned to be noticeably shorter than r_1^c for these metals. Our results are in good agreement with the recent report on liquid Ni. Using the molecular dynamics method the authors [5] detected the shortening of the atomic distance by 15-20 % in clusters as compared with the r_1^c value.

As to RDF curves simulation the first coordination maximum of the discussed metals can be modeled well taking into account the single shortest distance value only. Nevertheless, the RDF first maximum cannot give the detailed representation of the inside structure of the first atomic coordination.

4. References

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